Barrier Degradation in Aluminum Metallized Polypropylene Films

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ABSTRACT

The oxygen transmission rate (OTR) and moisture vapor transmission rate (MVTR) in metallized oriented polypropylene films are influenced by the surface properties of the polymer film and the characteristics of the deposited aluminum layer. Lack of barrier properties after metallization and degradation of the barrier quality after laminating and bag forming, can be related to the quality of the film surface and the conditions under which the metallization process is performed. Metallizing parameters such as pressure conditions in the vacuum chamber, thermal load on the polymer surface and mechanical effects resulting from the thickness of the metal coating and web tension, are shown to play a key role in determining barrier quality. The magnitude of the effect of such parameters depends not only on the process conditions but also on the basic design of the metallizing equipment.

Basic data on pinhole density, aluminum cracking as a function of film elongation, micrographs, OTR and MVTR measurements, are used to demonstrate how barrier quality can be influenced by web coating speed, boat distance to the film surface, web tension, functionality of the film surface, and the actual thickness of the aluminum layer. As a result, barrier quality of a given metallized film can range from poor to excellent, based on the equipment in which it is processed, the process conditions, the optical density of the metal layer and additional functionalization that can be imparted to the film surface in the metallizer by plasma treatment and polymer coating.

BARRIER DEGRADATION DUE TO THE QUALITY OF POLYPROPYLENE FILM

The condition of the polypropylene surface is a key factor in determining the mechanical properties and level of oxygen and moisture barrier of the aluminum layer. Low molecular weight material on the film surface due to oxidation can create volatile material that can boil off during aluminum deposition, creating pinholes and poor metal adhesion. Low level of surface functionalization of the polymer film will also reduce metal adhesion and degrade the crystal structure of the aluminum layer [1]. Furthermore, the surface of the polypropylene film can have residual absorbed air and moisture that are present during the metallization process. The moisture leads to the formation of a hydrated aluminum oxide, which does not provide the same level of corrosion protection as a conventional aluminum oxide formed in dry ambient conditions. This leads to higher OTR and MVTR, and reduced resistance to aluminum corrosion under normal application conditions.

The effect of poor film surface properties on the metallization layer can be summarized as follows:

- Increased amount of pinholes
- Poor adhesion between aluminum layer and polypropylene film surface
- Poor nucleation and crystal structure of aluminum layer
- Reduced sticking coefficient, i.e. lower optical density (OD)
- Poor barrier after metallization
- Rapid barrier degradation after lamination and bag making

To ensure high quality polypropylene film, the molecular weight distribution and the amount of additives in the polypropylene resin should be controlled by the manufacturer. Additives and sealant layer material should be limited to the non-metallized film surface only. Transfer of such foreign materials to the metallizable surface can create nucleation sites that degrade the barrier properties of the aluminum layer.

Functionalization of the film surface can significantly enhance the polypropylene surface properties, leading to improved metal adhesion and barrier properties [1]. The film surface can be functionalized using one or more methods that include:

- Co-extrusion or coating of the film surface with a thin functional skin
- In-line flame or corona treatment in air
- Corona treatment in a controlled atmosphere
- In-line plasma treatment during the metallization process

Flame and corona treatment are incorporated in the film production process. Co-extruded functional skins can be applied during the film manufacture, or in post coating processes, prior to metallization, or inline with the metallization process in the vacuum chamber [1,2]. Plasma treatment can also be performed inline with the metallization process.

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VACUUM EFFECTS

The quality of the aluminum layer is affected by the operating vacuum during the matallization process. High ambient pressures that are greater than about 2-4$\times10^{-4}$ Torr, can adversely effect the quality of the aluminum coating. At higher pressures, a significant amount of the aluminum is reacted with air and moisture. This results in a contaminated aluminum lattice which has many ramifications, including poor adhesion between the aluminum layer and the polypropylene film surface, poor barrier response to elongation, higher electrical resistivity, lower corrosion resistance, and poor short and long term barrier quality. To assure proper pressure measurement, pressure sensors should be located near the process zone and as far as possible from the diffusion pump. A Residual Gas Analyzer (RGA) should be used to detect the presence of water vapor.

A tight aluminum evaporation boat box is also desired to keep the partial pressure of the aluminum vapor constant and directed upward towards the film surface. In commercial metallizers that operate at high web speeds, much of the aluminum deposition is taking place in a non line-of-sight manner, due to the high vapor pressure of the evaporated aluminum. A boat box with open side walls will allow aluminum to deposit all over the chamber, and also ambient gas to infiltrate and contaminate the aluminum cloud. A closed boat box can improve the quality of the deposited aluminum layer when the vacuum conditions in the chamber are less than perfect.

EFFECTS OF THERMAL LOAD ON FILM

The thermal load on the propylene film that results from the infra red heat of the intermetallic boats, can be significantly more damaging than the heat transferred to the film from the aluminum vapor. This was first demonstrated by conducting a metallization experiment in a box coater, in which the amount of deposited aluminum was kept constant while the heat from the evaporator was varied (seeFigure 1).

Source Distance to Film	Optical Density	# of Pinholes Per Unit Area
4"	2.0	Very High
14"	2.0	Virtually None

Figure 1 Box coater experiment to determine effect of thermal load on pinholes

The infra red heat from the source or boats is inversely proportional to the square of the distance. Therefore, as the boat distance is increased the thermal load is decreased, which apparently decreases the number of pinholes.

The thermal load is also proportional to the web speed during the metallization process. As the web speed increases, the amount of thermal heat that the film sees is decreased, thereby decreasing the number of pinholes (see Figure 2).

An indirect method of measuring the quality of the metallized films is by conducting a resistive elongation test. In this test the increase in resistance of the metallized film is measured as a function of percent elongation. The degree of microcracking as the film elongates has been related to an increase in the OTR and MVTR values. Figure 3 shows that aluminum matallized coatings deposited at higher web speeds are more resistant to cracking as a function of elongation.

Although a chill roll subsequent to the metallization station is used to remove heat from the wound film, high thermal loads can activate the sealant on the back side of the film. This causes the film to adhere to itself upon winding, which is also known as blocking of the rewound roll. Roll blocking will create pinholes, which lead to poor barrier properties.

Film Speed (ft/min)	Optical Density	# of Pinholes
150	2.0	2.5X
500	2.0	X

Figure 2 - Effect of web speed on pinhole count

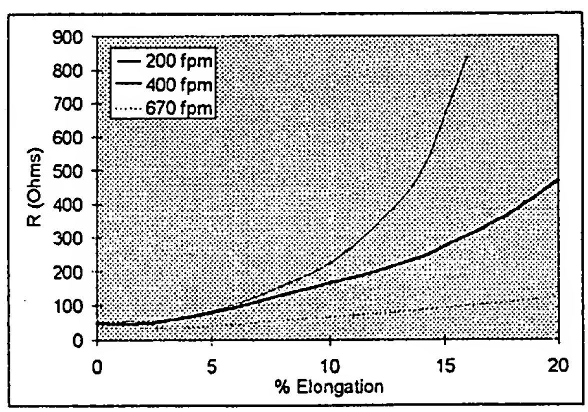

Figure 3 - Resistive elongation tests of OPP films metallized with the same OD and varying web speeds. In this experiment the boat power was the same, while the wire feed was varied to produce the same OD at different thicknesses.

Higher temperature films such as polyester are not as sensitive to thermal loads. Similarly, polypropylene film can resist thermal degradation, when coated with high temperature skins such as multifunctional acrylate polymers [2]. Figure 4, shows that

acrylate coated OPP film has significantly lower number of pinholes for a given set of metallizing conditions.

Film Type	# of Pinholes per Unit Area
OPP + Al	1760
OPP + Acrylate + Al	590

Figure 4 - Effect of acrylate coating on pinhole count

FREE SPAN VS. SUPPORTED WEB METALLIZATION

Recently there has been considerable evidence that metallized films can have superior barrier properties when metallized in an unsupported web format. Some potential explanations that have been put forward include the following: (1) A large thermal gradient develops between the drum and metallized surface due to a hot film surface being supported by a chilled drum. This thermal gradient may cause microcracking in the aluminum layer, which can increase the OTR and MVTR values of the metallized film. (2) The drum is reflecting a significant amount of infra red heat back into the film, thereby causing the thermal load on the film to greatly increase. (3) The thermal load is higher in free span metallizing but somehow this is beneficial to the quality of the metal layer.

After investigating some of the reported observations, we found that the configuration of the free span metallizers was significantly different. Specifically the distance of the resistively heated boats to the film surface is about double of that of most supported systems. As shown below, this results in a lower thermal load to the film (contrary to common belief, item 3 above). Figure 5 shows the thermal load on the OPP film surface for typical free span and supported metallizer systems. It is noted that the free span metallizer reduces the thermal load about 33% compared to the conventional supported metallizer. This thermal load reduction is due mostly to the increased boat distance from the film, even though the metallization window area is doubled in the free spanmetallizer.

MECHANICAL EFFECTS

Aluminum layer damage and subsequent loss of barrier properties can be induced by various mechanical effects including high web tension, metal abrasion and high aluminum thickness. Web tension problems are fairly well understood.

Film	# of Pinholes Per Unit Area
PP + Al film	1760
PP + Al + acrylate	350

Figure 6 - Reduction of abrasion induced pinholes by acrylate coating of the aluminum layer

High web tension is a common cause of poor barrier, due to aluminum metal microcracking and creation of pinholes in the aluminum layer. The effect of abrasion on the aluminum layer can be demonstrated by coating the metallized film with a vacuum deposited acrylate coating immediately after the metal deposition and before the film contacts any rollers. As shown in Figure 6, the number of abrasion induced pinholes on the acrylate coated metal layer is significantly less.

Aluminum thickness problems are less understood. Most metallizing converters metallize packaging films to about the same optical density, favoring thicker coatings to assure better barrier properties. Our observations suggest that the relationship between metal thickness and barrier properties is rather complex, and that an optimum aluminum layer thickness exists, that maximizes OTR and MVTR. Figure 7, shows that metallized aluminum layers become more brittle as the thickness increases. This suggests that thinner films will produce better barriers. However, at some lower thickness the metal coating starts to transmit gas and vapor.

Device	Boat-Film Distance	Metallization Window	Heat from Condensation cal/cm^2	Radiant Heat cal/cm^2	Total Heat cal/cm^2	Thermal Load Reduction
Conventional Supported Metallizer	7"	10"	0.0141	0.0203	0.0344	0%
Free Span Metallizer	15"	20"	0.0141	0.0089	0.0230	33%

Figure 5 - Comparison of thermal load on OPP film from free span and supported metalizers.

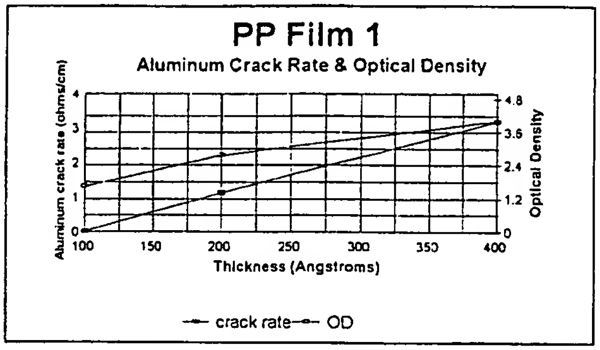

Figure 7 - Aluminum cracking rate and optical density as a function of Al thickness

The lower thickness limit is a function of the physical and chemical properties of the film surface, as well as the metal deposition conditions. Figure 8, shows schematically that beyond the optimum thickness limit, the measured OTR is a function of film handling, which includes unwinding, laminating, and bag forming. Therefore, one can be misled when measuring barrier properties of thick aluminum layers immediately after metallizing, and prior to subsequent processes that can induce mechanical stress. Figure 9, shows OTR data for a metallized OPP film, with metal OD around the optimum value.

Typical Behavior of OTR and MVTR of Most Al Metallized PP Films

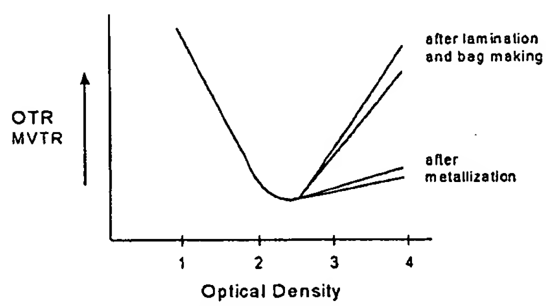

Figure 8 - Schematic representation of OTR as a function of OD. At higher aluminum thicknesses, the measured OTR can change significantly with film handling.

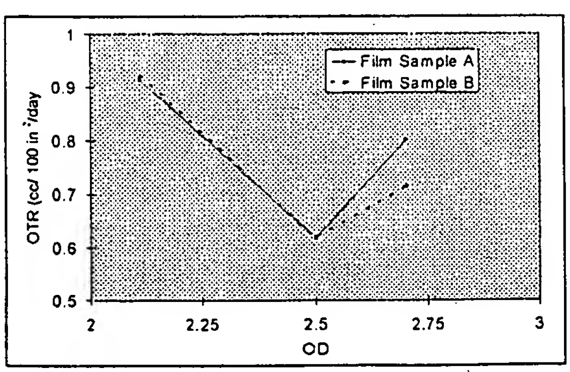

Figure 9 - OTR as a function of OD for two different metallized OPP films. This data shows that the optimum OD is in the range of 2.1 to 2.6.

Figure 10, shows "microcracks" on metallized OPP film that are produced by film elongation. Note that the aluminum layer is apparently stretched and deformed in somewhat uniform fashion perpendicular to the stretch axis. This behavior is a function of the physical and chemical properties of the film surface.

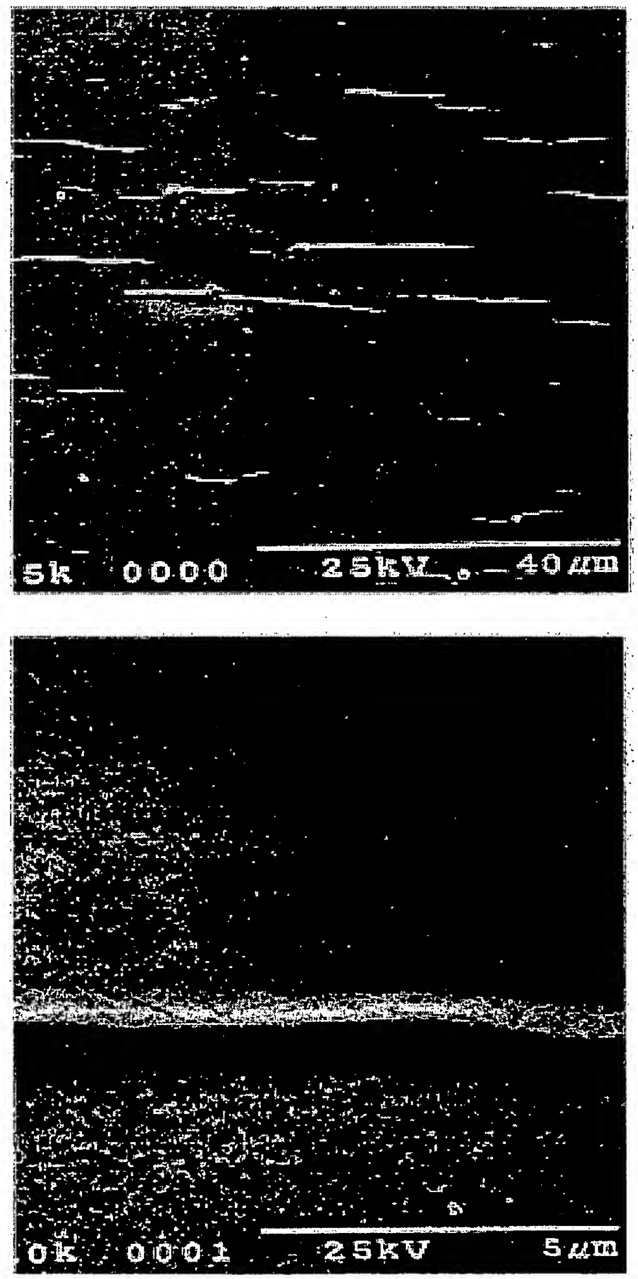

Figure 10 - Effect of polypropylene film elongation on the metallized aluminum coating. Such deformation of the metallized film becomes visible at about 15-20% elongation.

Solutions to the aforementioned adverse effects include optimization of the aluminum thickness for a given film to avoid microcracking in the aluminum layer, Periodic metallization and measure of OTR and MVTR of a control low gage film to test the web tension system, and plasma treatment and polymer coating of the film.

Plasma treatment of the film prior to deposition of the aluminum layer followed by overcoating with an acrylate significantly reduces the tendency of the aluminum layer to undergo microcracking upon deformation. The tendency of metallized film to microcrack can be routinely monitored by measuring electrical resistance as the film is elongated. Figure 11 shows the effect of plasma treatment and polymer coating on the microcracking of the metallized layer.

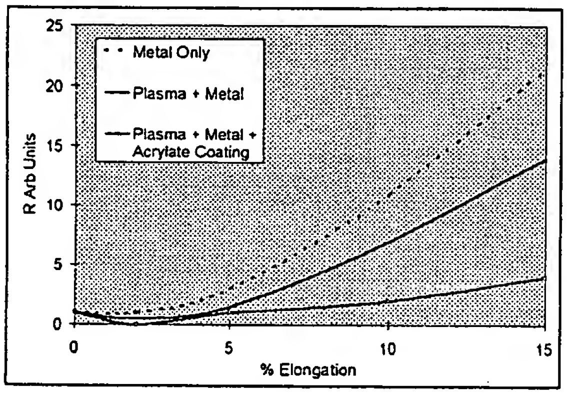

Figure 11 - Typical resistive elongation test results for a low-end metallizable OPP film, with plasma treatment prior to metallization and with acrylate coating over the metal layer.

CONCLUSIONS

The level of oxygen and moisture barrier in a metallized polypropylene film and vulnerability of the barrier to degradation are primarily affected by the following parameters:

- functionality of the polypropylene surface
- vacuum conditions during the metallization process
- thermal load on the film
- mechanical effects on the metallized web.

REFERENCES

1. A. Yializis, R. E. Ellwanger, and A. Boufelfel, "Superior Polymer Webs via *in situ* Surface Functionalization," 39th Annual SVC Conference, pp 384, 1996.
2. A. Yializis, "High Oxygen Barrier Polypropylene Films Using Transparent Acrylate-A12O3 and Opaque Al-acrylate Coatings," 38th Annual SVC Conference, pp 95, 1995.